

# Magnesium Corrosion Characterization and Prevention

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**Oak Ridge National Laboratory**

**National Transportation Research Center**

**2018 U.S. DOE Vehicle Technologies Office**

**Annual Merit Review**

**June 19, 2018**

**Project ID: mat113**

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# Project Programmatic Overview

## Timeline

- Project Start: Oct. 2015
- Project End: Sept. 2018
- ~70% Complete

## Budget

Total Budget: \$1150K

- \$400K received FY16
- \$360K received FY17
- \$390K anticipated FY18 (\$50k received through Q2)

## Barriers

- 50% vehicle body/chassis weight reduction stretch goal will require low-cost, corrosion-resistant Mg alloys
- Maintenance, Repair, and Recycling of Mg alloys
- Performance (corrosion resistance) of Mg alloys

## Partners/Collaborators

- Magnesium Elektron North America
- Henkel Corporation
- McMaster University
- Magna International
- McGill University
- University of Manitoba
- U. Tenn. Space Institute

# Relevance/Objective: Fundamental Understanding of Mg Corrosion for Improved Mg Alloys +Coatings

**OBJECTIVE:** Better understanding of how Mg alloying changes corrosion film growth and coating formation to provide basis for better Mg alloys/coatings to permit wider use of Mg for lightweight vehicles

## **Relevance:**

- Mg alloys of interest to automotive manufacturers: low density, good strength, amenable to casting, recyclable
- Mg alloys rarely form continuous and fully protective surface film making alloys susceptible to corrosive attack
- Alloying shown to modify corrosion film formation and impact protection of reactive-based coatings

# Milestones: FY18 Focus on Coatings

Complete electrochemical screening of bare and Henkel BONDERITE electro-ceramic coated AZ31B, AZ91, ZE10A, WE43	Quarterly	12/31/2017	Complete
Complete initial attempt at D penetration/TOF-SIMS cross-section imaging assessment from a NaCl + D <sub>2</sub> O exposure (bare alloy)	Quarterly	3/31/2018	Complete
Complete aqueous corrosion study of bare and Henkel BONDERITE electro-ceramic coated ± top coated AZ31B, AZ91, ZE10A, WE43	Quarterly	6/30/2018	In Progress
Submit at least 1 paper on findings from the bare and coated AZ31B, AZ91, ZE10A, and WE43 study	Quarterly	9/30/2018	In Progress
Submit at least 1 paper on findings from in-situ SANS and TOF-SIMS characterization of NaCl + D <sub>2</sub> O exposures	Stretch	9/30/2018	Future
Submit at least 1 paper on D penetration from D <sub>2</sub> O exposure (SIMS and/or TOF-SIMS) for high second phase content Mg alloys selected among WE43, AZ91, and Mg-Zn-Ca-Nd model alloys	Stretch	9/30/2018	Future
Determine if in-situ small angle neutron scattering (SANS) of Mg corrosion is feasible, adds additional insights beyond ex-situ studies	Go/No Go	12/31/2017	*Delayed

\*CR resulted in delayed funding. In-Situ/Ex-situ bare alloy SANS data successfully obtained but not yet fully analyzed. Available funds focused on coating characterization efforts.

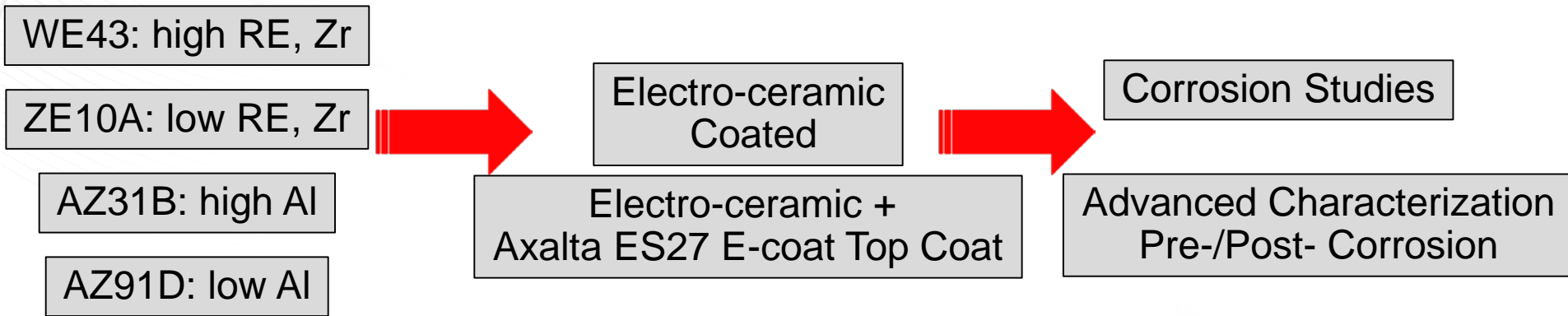


# Approach: Fundamental Study of State-of-the-Art Mg Alloys + Coatings to Address Corrosion Barriers

- **Automotive-relevant commercial/model alloys (w/ Magnesium Elektron)**
  - **Mg-Al type**: wrought **AZ31B-H24** (~Mg-3Al-1Zn), cast **AZ91D** (~Mg-9Al-1Zn)
  - **Zr/RE (rare earth) type**: wrought **ZE10A** (~Mg-1.5Zn-<0.5 Zr+Nd), wrought **WE43** (~Mg-4Y-3RE->0.2Zr)
  - **Model cast Mg and Mg-X alloys** (X = Al, Zr, Nd, Ca, Zn) (Ca alloys from McGill)
- **Automotive-relevant coatings (w/ Henkel Corporation)**
- **Focus on how alloying additions influence:**
  1. bare alloy corrosion film growth (FY2016/2017)
  2. coating formation and subsequent corrosion resistance (FY2017/2018)
- **New insights from use of advanced characterization techniques not previously widely applied to Mg corrosion:**
  - analytical electron microscopy of film/coating cross-sections and interfaces
  - mass spectrometry (SIMS, TOF-SIMS, APT): use of D<sub>2</sub>O and H<sub>2</sub><sup>18</sup>O tracers
  - neutron scattering at ORNL Spallation Neutron Source + High Flux Isotope Reactor
- **Integration of industrial partners into team provides path to transfer fundamental findings to practice**

# Approach: Systematic Coating w/Same Conditions on Previously Characterized Range of Mg Alloys

How alloy substrate influences coating formation and performance?



## •**Corrosion Studies** (led by Kish, McNally of McMaster U.):

- mass loss/hydrogen evolution
- potentiodynamic polarization
- scanning vibrating electrode technique (SVET), localized electrochemical impedance spectroscopy (LEIS)

## •**Characterization** (ORNL: interface morphology micro-/nano -segregation):

- 3D microscopy
- Cross-section scanning transmission electron microscopy (STEM/EDS)
- D<sub>2</sub>O exposure/TOF-SIMS Imaging

# Key Technical Accomplishments and Progress Since FY2017 Review

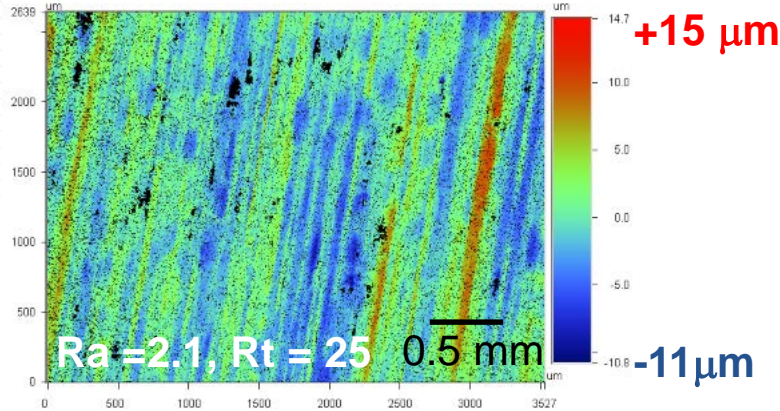
- Completed analytical electron microscopy of as electro-ceramic coated and electro-ceramic coated + e-coat top coat for AZ31B, AZ91D, ZE10A, WE43 (focus of this presentation)
- Completed corrosion exposures for bare alloy, electro-ceramic coated, and electro-ceramic coated + e-coat top coat AZ31B, AZ91D, ZE10A, WE43
- 24 h in-situ small angle neutron scattering (SANS) of Mg corrosion in D<sub>2</sub>O + 5 wt.% NaCl to follow formation/degradation of film. Ex-situ SANS controls also analyzed by time-of-flight mass spectrometry (TOF-SIMS) (ZE10A, AZ31B) (extra slides, ORNL FY17 and FY18 activity)
- 2018 TMS LMD Magnesium Technology Award - Best Poster
- Paper: *“Rapid Diffusion and Nano-Segregation of Hydrogen in Magnesium Alloys from Exposure to Water”*, ACS Applied Materials & Interfaces, 9 (43), 38125-38134 (2017) (focus of last year’s presentation)



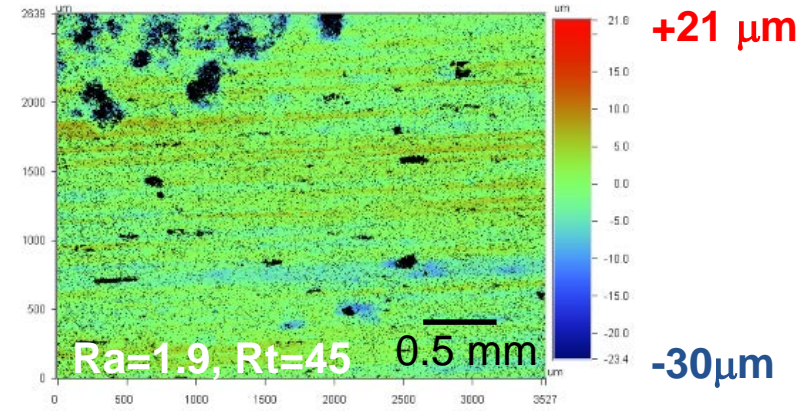
# Technical Progress FY18: Zr + RE in Alloy Promote Rougher Coating Surface

## 3D Surface Microscopy of As Electro-ceramic Coated Alloys

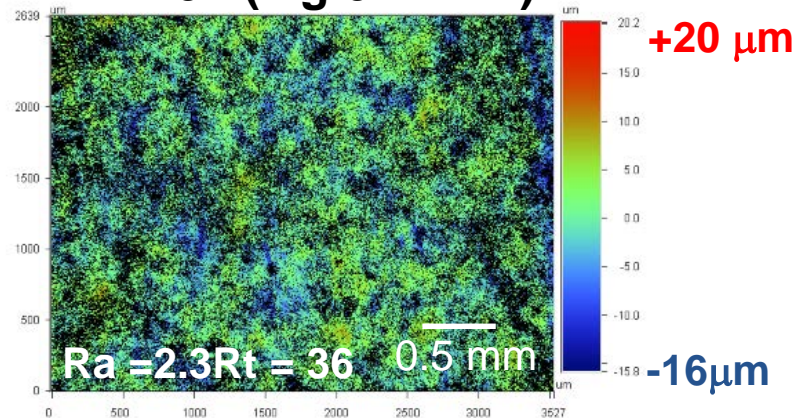
AZ31 (Mg-3Al-1Zn)



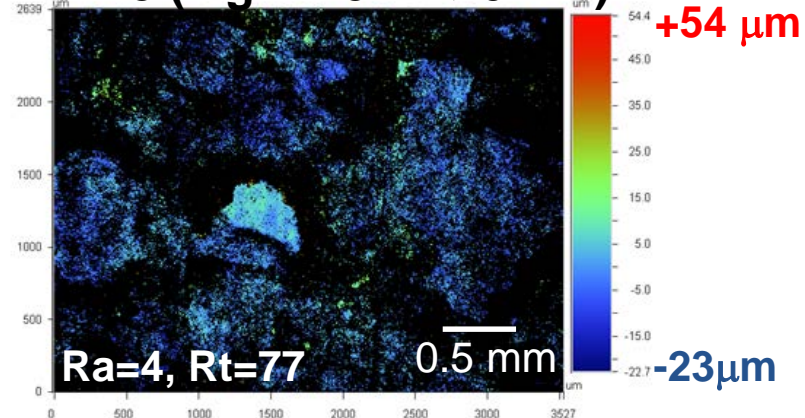
ZE10A (Mg-1.5Zn-<0.5 Zr+Nd)



AZ91 (Mg-9Al-1Zn)



WE43 (Mg-4Y-3RE->0.2Zr)



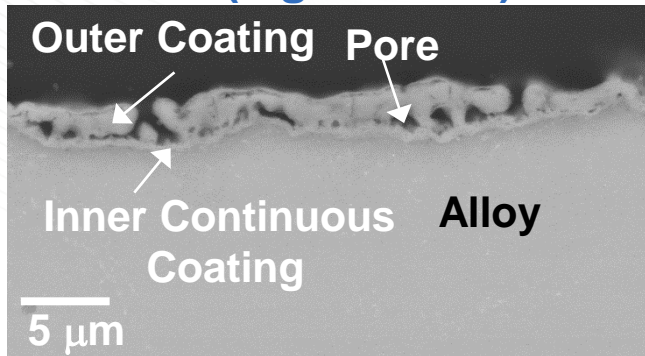
- Roughness may be beneficial for subsequent top coat adherence
- Ra = average roughness, Rt = max profile height difference



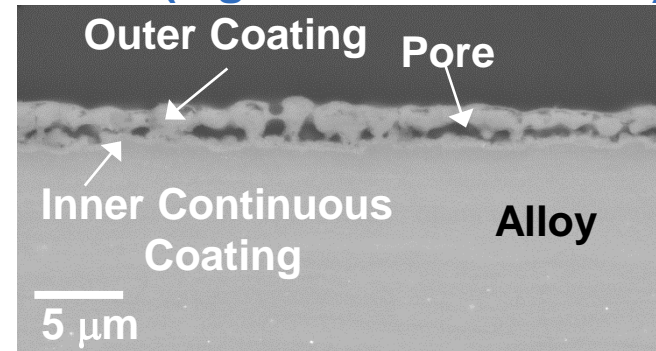
# Technical Progress FY18: Higher Al, Zr + RE in Alloys Generally Promote Thicker Coatings

## SEM Cross-Sections of As Electro-ceramic Coated Alloys

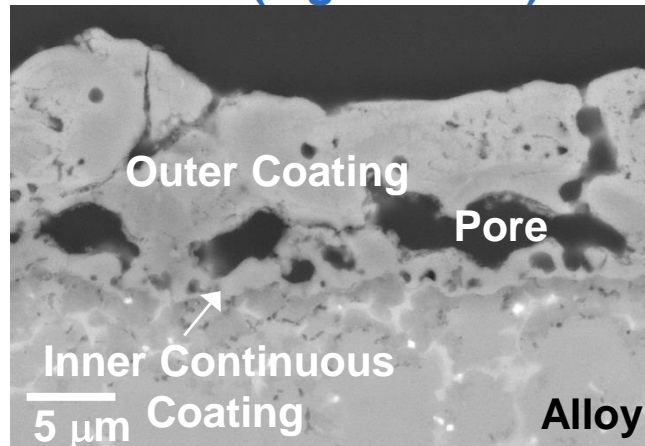
**AZ31 (Mg-3Al-1Zn)**



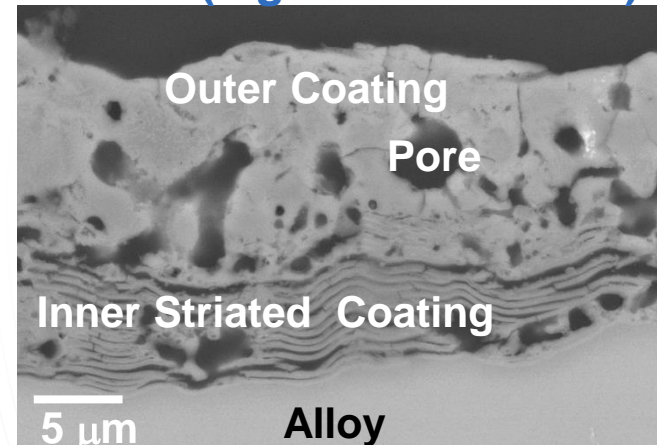
**ZE10A (Mg-1.5Zn-<0.5 Zr+Nd)**



**AZ91 (Mg-9Al-1Zn)**



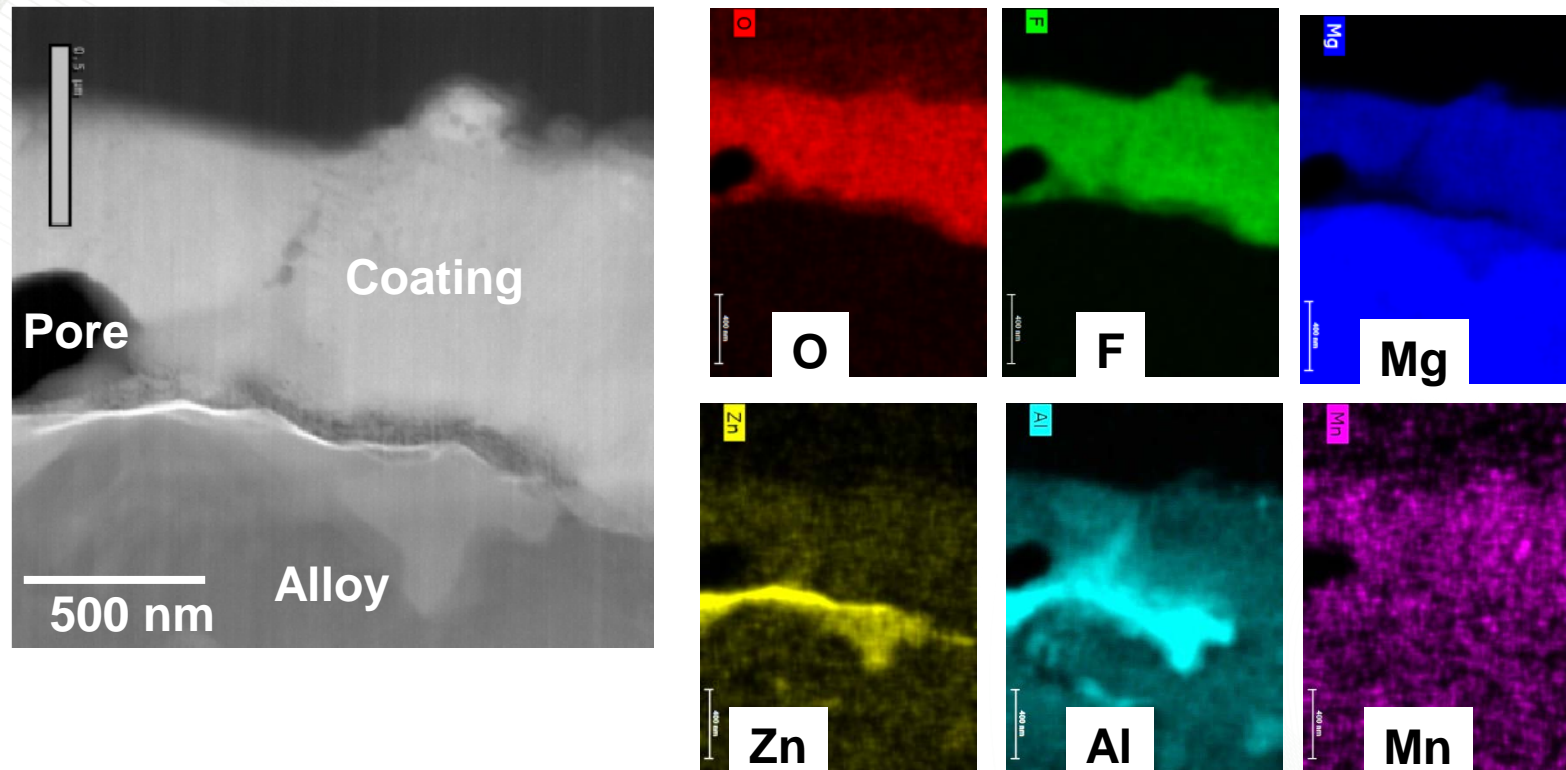
**WE43 (Mg-4Y-3RE->0.2Zr)**



- WE43: unexpected striated inner layer morphology
- Thickness variability observed for ZE10A, AZ91, WE43

# Technical Progress FY18: Al Incorporation into $\text{Mg}(\text{F},\text{O})_2$ Electro-Ceramic Coating on AZ Alloys

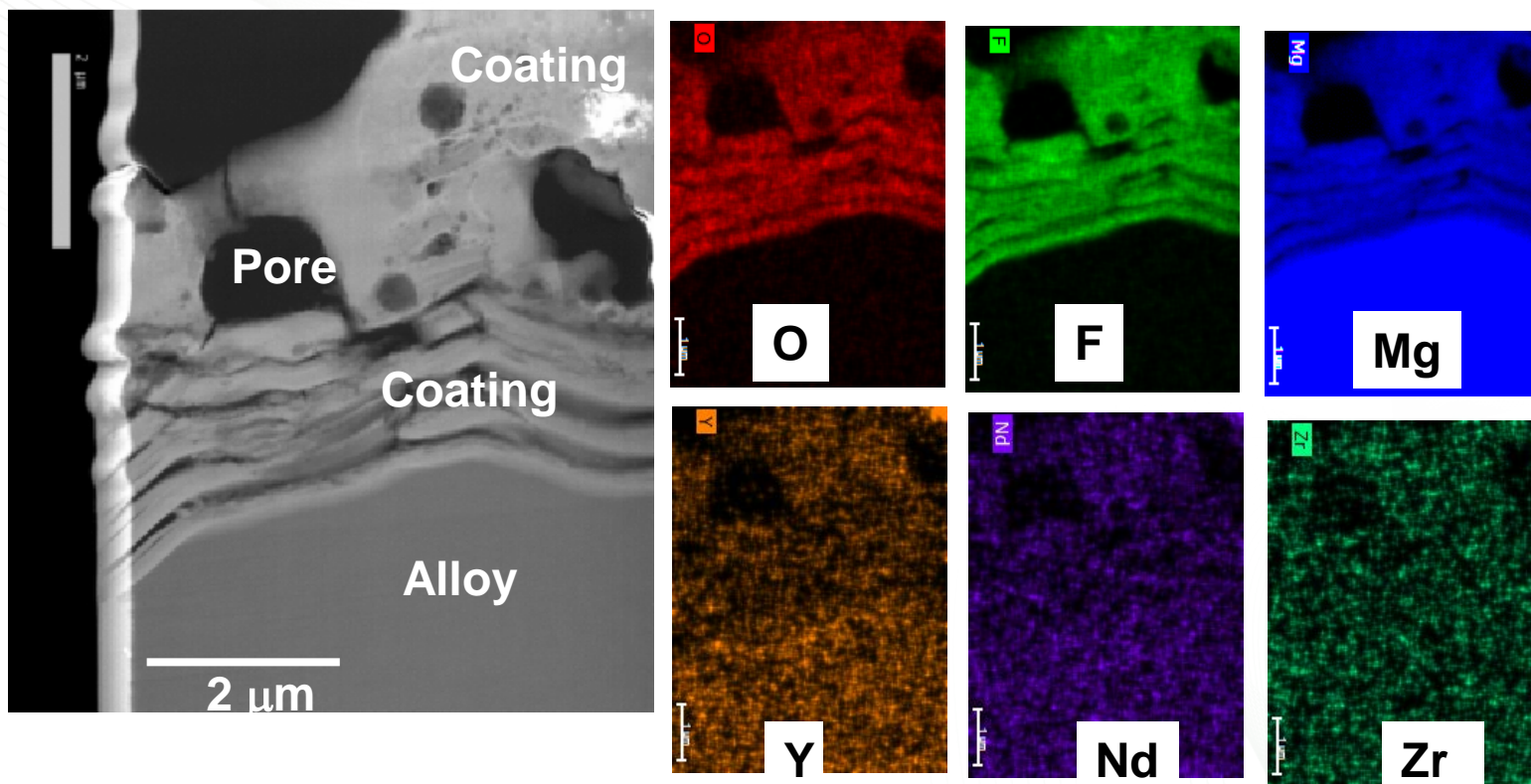
## STEM Cross-Section + Elemental Maps of Electro-ceramic Coated AZ91



- Electro-ceramic coating consistent with partially oxidized  $\text{MgF}_2$ -type phase  
--~40Mg-40F-(5-10)O at.% base (XPS)
- Al (few %) from alloy in coating + Zn enrichment at alloy-coat interface.  
Similar segregation seen in  $\text{H}_2\text{O}$ -formed films on uncoated AZ31B, AZ91D  
-may benefit corrosion resistance

# Technical Progress FY18: No Zr, RE Incorporation into $\text{Mg}(\text{F},\text{O})_2$ on WE43, ZE10A

## STEM Cross-Section + Elemental Maps of Electro-ceramic Coated WE43

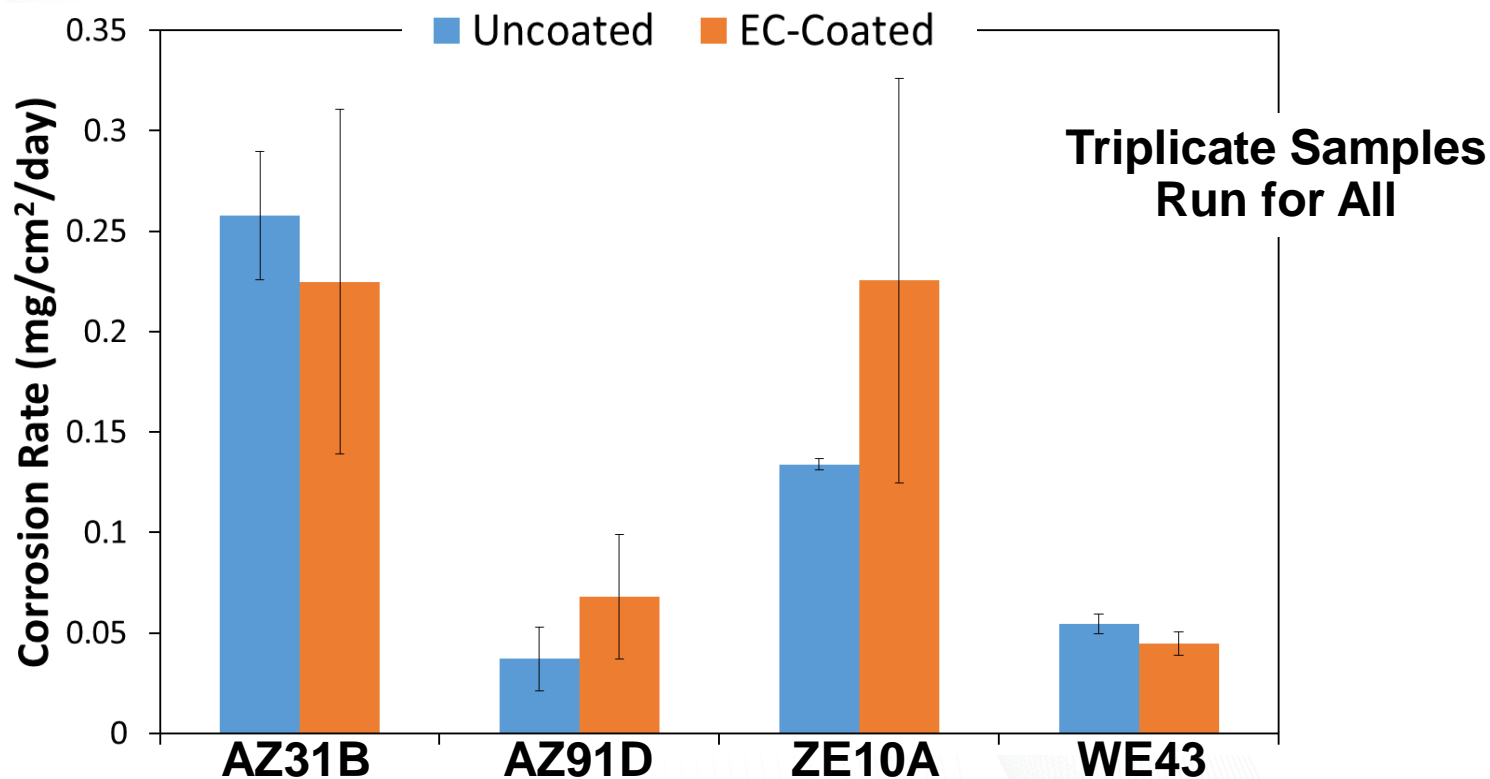


- Similar electro-ceramic coating chemistry to AZ alloys for WE43 and ZE10A
- No Zr, RE at/into electro-ceramic coating (where 2<sup>nd</sup> phase particles go?)
- Uncoated WE43, ZE10A corrosion films tend to trap 2<sup>nd</sup> phase particles + RE alloy-film interface enrichment



# Technical Progress FY18: Large Scatter, No Corrosion Benefit for Electro-ceramic Coating Alone

Corrosion Rates Calculated from H<sub>2</sub> Evolution Measurements in Quiescent 0.1 M NaCl (aq) 7 day Immersion at Room Temperature

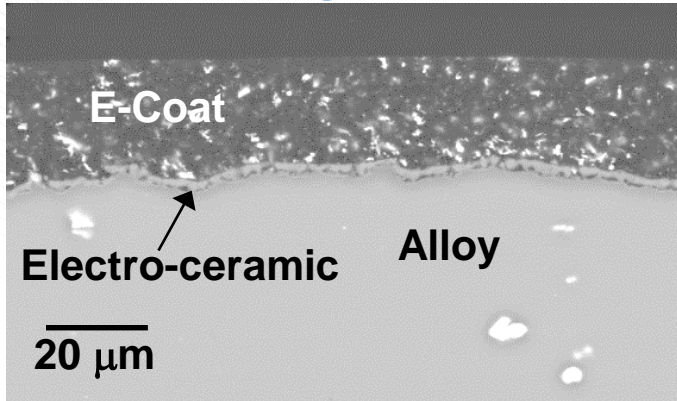


- Moderate benefit of coating was observed in potentiodynamic polarization (extra slides), but was not maintained in aggressive 7 day immersion test
- Electro-ceramic intended as part of multi-layer Mg coat system, not prime reliant (coating resistance trended with bare alloy resistance)

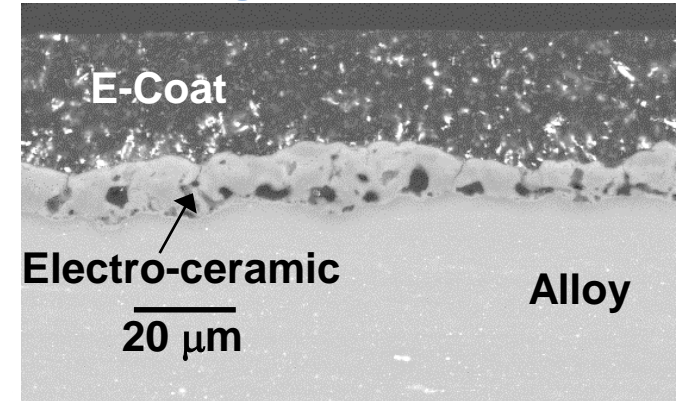
# Technical Progress FY18: Electro-ceramic Layer Preserved after Subsequent E-Coat Top Coat

## SEM Cross-Sections After Axalta ES27 Electrocoat

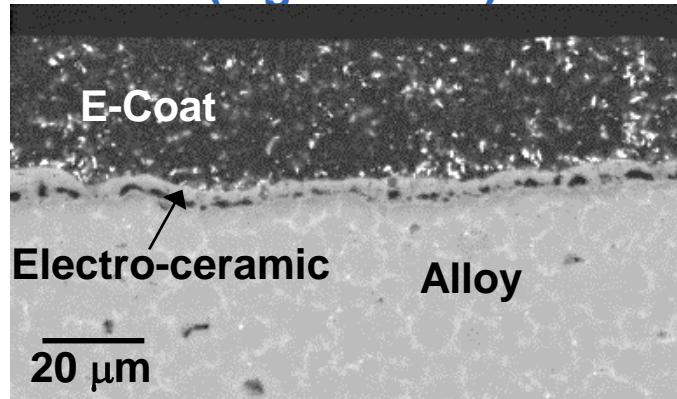
AZ31 (Mg-3Al-1Zn)



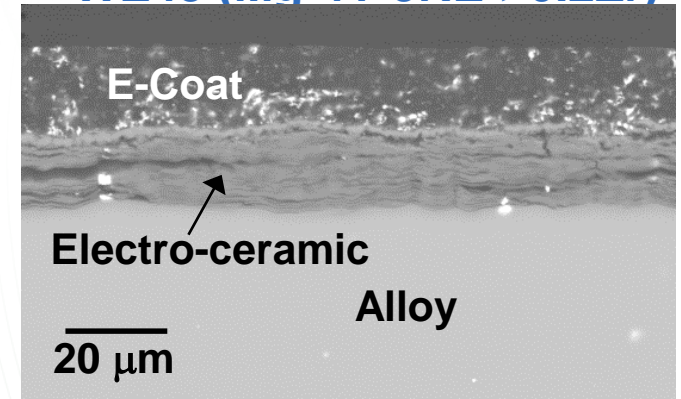
ZE10A (Mg-1.5Zn-<0.5 Zr+Nd)



AZ91 (Mg-9Al-1Zn)



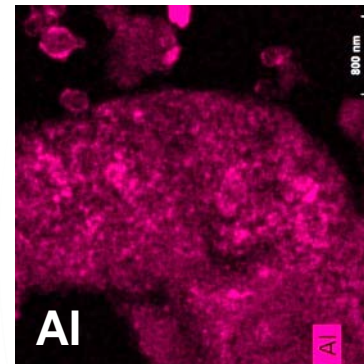
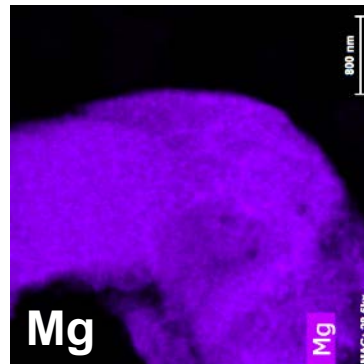
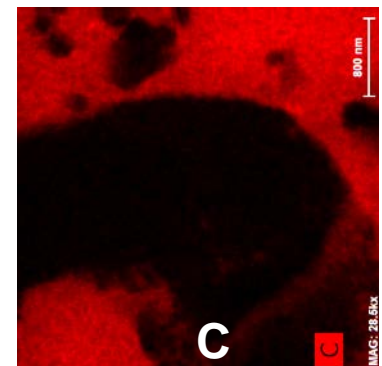
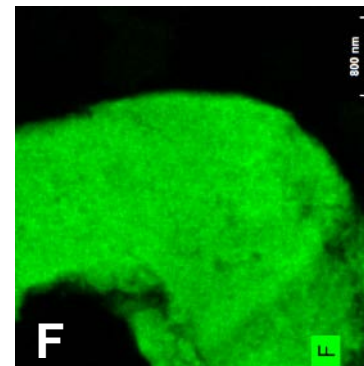
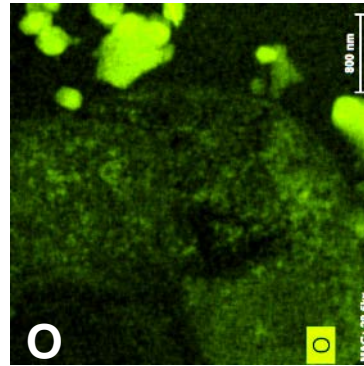
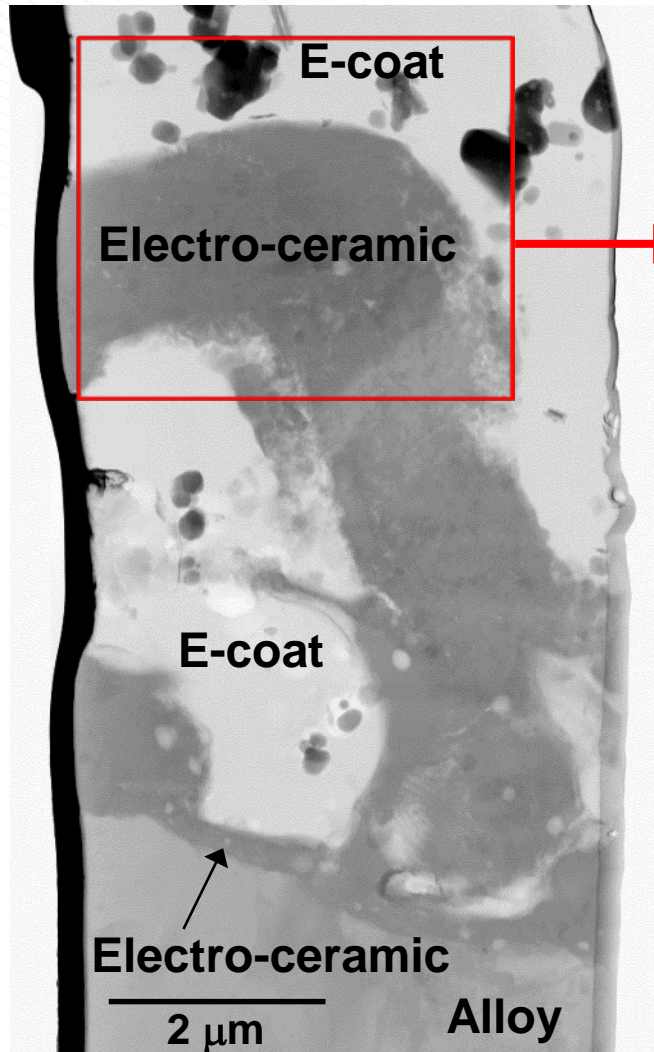
WE43 (Mg-4Y-3RE->0.2Zr)



- Inner electro-ceramic preserved after e-coat: aides adherence, corrosion resist
- Attack of conversion dip coats by e-coat process previously observed

# Technical Progress FY18: E-Coat Percolates into Porous Electro-ceramic Layer on AZ91

STEM Bright Field Cross-Section + Elemental Maps of Exalta ES27 E-coat on Electro-ceramic coated AZ91

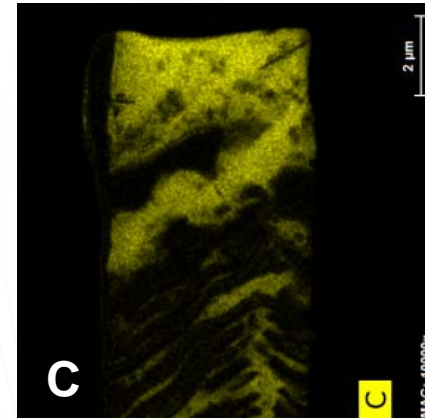
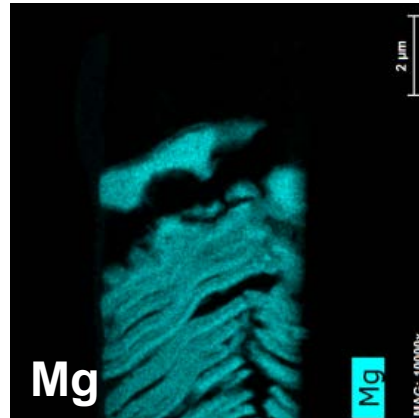
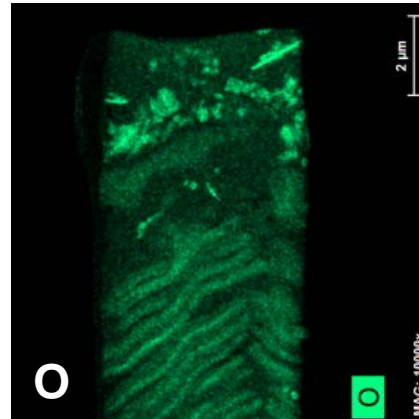
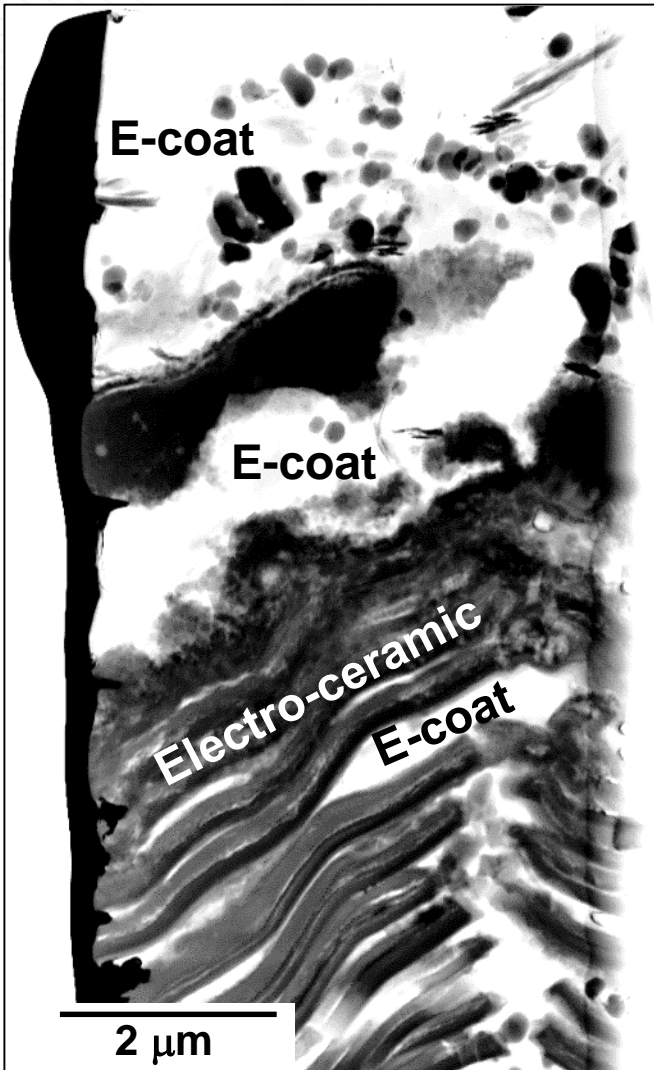


- Infiltration by e-coat helps adherence, protectiveness
- E-coat contains oxide particles in carbon-rich matrix



# Technical Progress FY18: E-coat Percolates into Thick Striated Electro-ceramic Layer on WE43

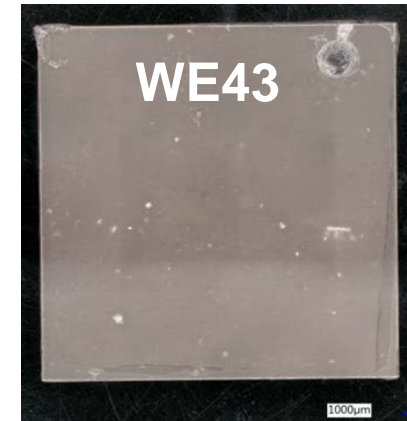
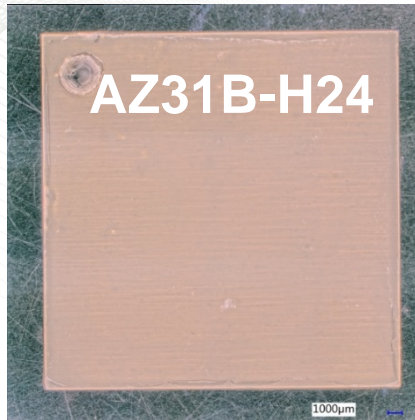
STEM Bright Field Cross-Section + Elemental Maps of Exalta ES27 E-coat on Electro-ceramic coated AZ91



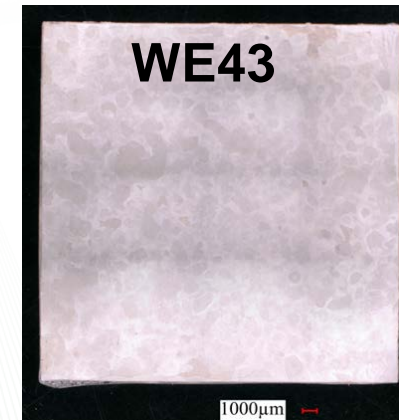
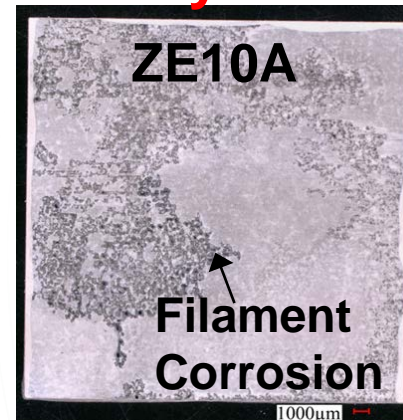
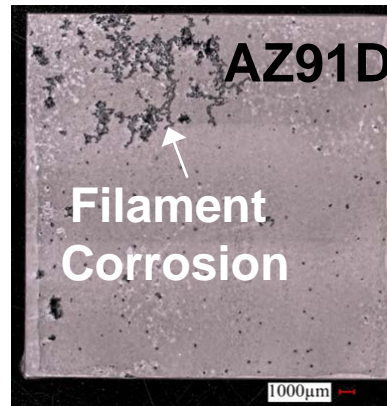
- No e-coat issues percolating throughout unusual striated inner electro-ceramic layers (beneficial?)

# Technical Progress FY18: No Attack of Electro-ceramic + E-Coat After 7 to 9 Days in 0.1M NaCl

## Electro-ceramic + E-Coat Top Coat



## Electro-ceramic Only



- $< 0.01 \text{ mg/cm}^2/\text{day}$  from  $\text{H}_2$  evolution measurements with e-coat top coat
- Study of scribed electro-ceramic + e-coat by scanning vibrating electrode technique, localized electrochemical impedance spectroscopy planned



# Coating Related Results and Conclusions

- Alloy substrates significantly impacted electro-ceramic coating formation:
  - Higher Al, Mg-alloys resulted in thicker coating
  - Higher RE, Mg-alloys resulted in thicker coating, striated morphology
- Al from the alloy substrates migrated into the electro-ceramic coating, whereas Zr/RE did not. Similar  $\text{Mg}(\text{F},\text{O})_2$  chemistry was formed on all alloys
- Extensive percolation of e-coat into the preserved, inner porous electro-ceramic layer results in a corrosion-resistant, 2-layer coating
- Planned electrochemical study of scribed defects in e-coated alloy by SVET and LEIS will be related to interfacial structures via STEM cross-sections
  - insights for optimization of alloy and coating to achieve maximal protection
  - STEM, etc. characterization findings can feed into future coating modeling efforts by industry and academia



# Response to Reviewers Comments

**We thank the reviewers for their time and thoughtful comments**

- Multiple comments about H penetration into Mg alloys during corrosion. Approach/results were thought novel, ?'s regarding mechanism, significance.

We now have TOF-SIMS D<sub>2</sub>O + NaCl tracer studies for 30 min. to 24 h (parallel study with in-situ/ex-situ SANS-see extra slides). Enhanced H/D penetration related to H active additions like Zr, Nd, Ca, and related to alloy nanostructure-paper published. Likely important for ductility, formability, and SCC, especially as Mg transitions to more load bearing use. Basis to optimize microstructure to getter ingressed H. May help improve modeling now know H ingress can quickly occur during corrosion.

- The reviewer noted that there is a lot of great scientific work but its applicability/relevance to commercial alloys is questionable.

Project studies current commercial alloys and coatings selected by industrial partners. Discovered H ingress can guide alloy composition + microstructure optimization. Coating work can help guide optimization of alloy composition or coating process for better protection. Alloy-coating interface characterization can feed into modeling. New experimental techniques demonstrated can be used by other groups for Mg corrosion.

- Questions regarding specific roles of collaborators

FY2018 characterization by ORNL, alloys, coatings selected + supplied by Magnesium Elektron, Henkel, with input from Magna. Coating corrosion by McMaster U.

# Collaboration & Coordination with Other Institutions

- ORNL Team: Researchers from several divisions and Spallation Neutron Source, High Flux Isotope Reactor, and Center for Nanophase Materials Sciences User Centers
  - M.P. Brady: metallurgy, corrosion, oxidation
  - D.N. Leonard: microscopy
  - H.M. Meyer III: surface chemist
  - K. Littrell: small angle neutron scattering
  - M.G. Frith, A.J. Ramirez-Cuesta, L.L. Daemen, Y. Cheng: inelastic neutron scattering
  - L. Anovitz: geochemistry (includes Mg-O-H systems)
  - G. Rother: geochemistry and neutron scattering
  - G. Song: Mg corrosion and electrochemistry (now at Xiamen University)
  - E. Cakmak: XRD
  - A. Levlev/O. Ovchinnicova: TOF-SIMS
  - D. Shin: computational thermodynamics
  - W. Guo, J.D. Poplawsky: Atom probe tomography
- Bruce Davis **Magnesium Elektron North America**: select/supply Mg alloys + coatings, experiment input
- John Kukalis, Bruce Goodreau, Omar Abu Shanab, Kirk Kramer **Henkel Corp**: select/supply coatings
- Mostafa Fayek, **University of Manitoba**: geochemistry, depth-profile SIMS
- Joey Kish, Beth McNally **McMaster university**: electrochemistry, corrosion, coatings
- Stephen Yue, **McGill University**: supplied Mg–Zn–Nd–Ca alloys
- Feng-Yuan Zhang, **UTenn. Space Institute**: in-situ optical imaging of corrosion
- Collaborators/Input:
  - Tim Skszek, **Magna International**: Input to frame project plans, emphasis on wrought alloys for their potential to expand Mg adoption to automotive sheet components

# Remaining Challenges and Barriers

- Correlation of corrosion behavior with coating interfacial structure and chemistry (alloy/electro-ceramic, electro-ceramic/e-coat)
  - post-corrosion characterization key, in-progress
  - scribed coating study to examine how well coating interfaces resist corrosion as a function of alloy substrate-coating effects?
- Demonstration of TOF-SIMS cross-section imaging to assessment of H/D penetration for electro-ceramic coated alloys
  - does technique provide additional insights?
- Completion of AZ31B and ZE10A bare alloy In-Situ/Ex-Situ SANS corrosion analysis + supporting TOF-SIMS and STEM
  - does in-situ SANS provide new insights beyond ex-situ findings?



# Future Work: Project Ends Sept 30, 2018

- Complete SVET, LEIS for coated AZ31B, AZ91D, ZE10A, WE43
- Complete STEM of post-corrosion coatings, compare w/as-coated
- TOF-SIMS of electro-ceramic coated ZE10A and AZ31B exposed in  $D_2O$  to assess for D penetration differences with bare alloys
- Complete data analysis for in-situ/ex-situ SANS on bare AZ31B and ZE10A in  $D_2O$  + 5 wt.% NaCl
- Multiple papers to disseminate findings

**Any proposed future work is subject to change based on funding levels. Project has experienced delays in funding due to CR, may request no-cost extension**

# Summary

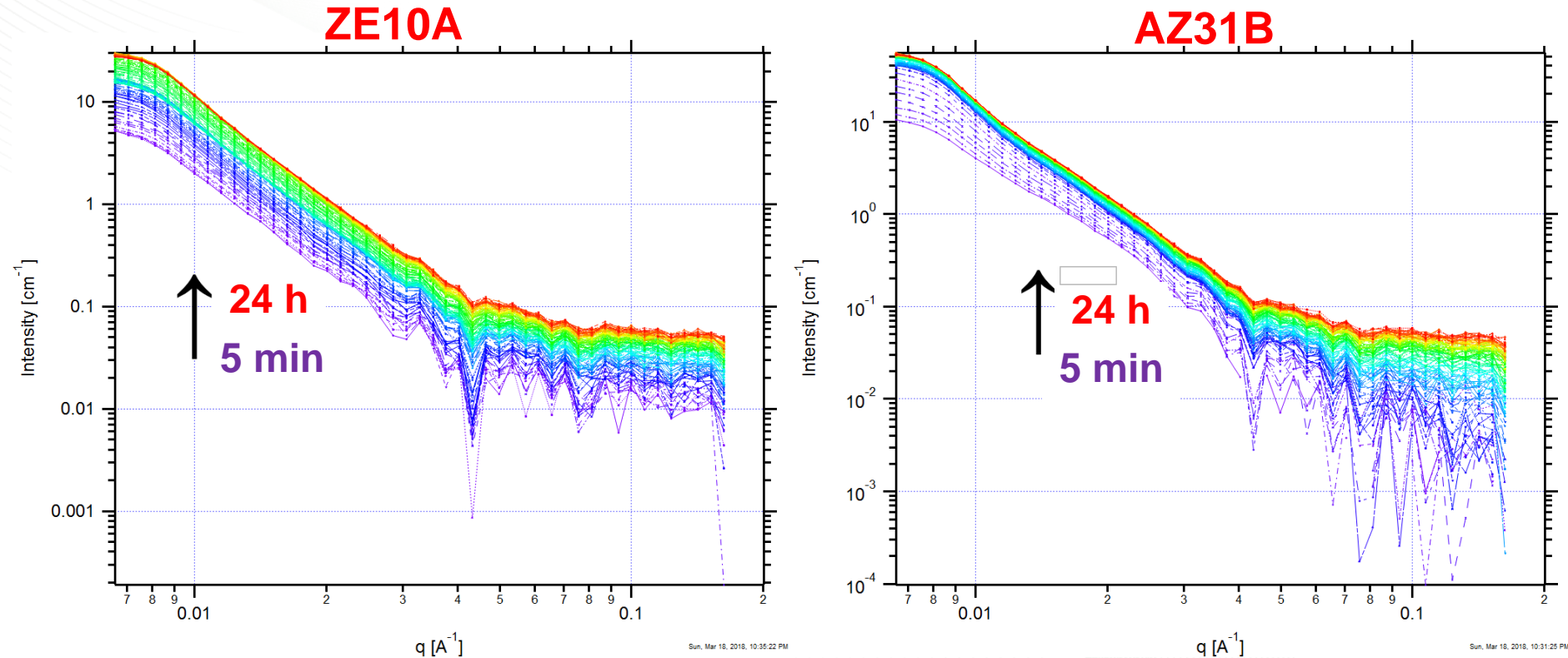
- **Relevance:** Corrosion key barrier to lightweighting with Mg
- **Approach:** New understanding via new characterization approaches to Mg corrosion. Provide future basis to improve corrosion resistance
- **Collaborations:** Mg alloy producer (MENA), Mg Coating Producer (Henkel), Input from Tier 1 supplier (Magna) along with multiple ORNL and university researchers for advanced characterization
- **Technical Accomplishments:** Systematic study of effects of alloy substrates on coating chemistry, morphology, and interfaces. Ongoing assessment of D<sub>2</sub>O tracer  $\pm$  NaCl, TOF-SIMS, and in-situ SANS to study Mg corrosion.
- **Future work:** Complete post-corrosion coating characterization, including scribed coatings. Complete TOF-SIMS and SANS assess. Publish findings: basis for new alloy/coating design strategies; new insights to feed into corrosion modeling by industry and academia

# Technical Back-Up Slides



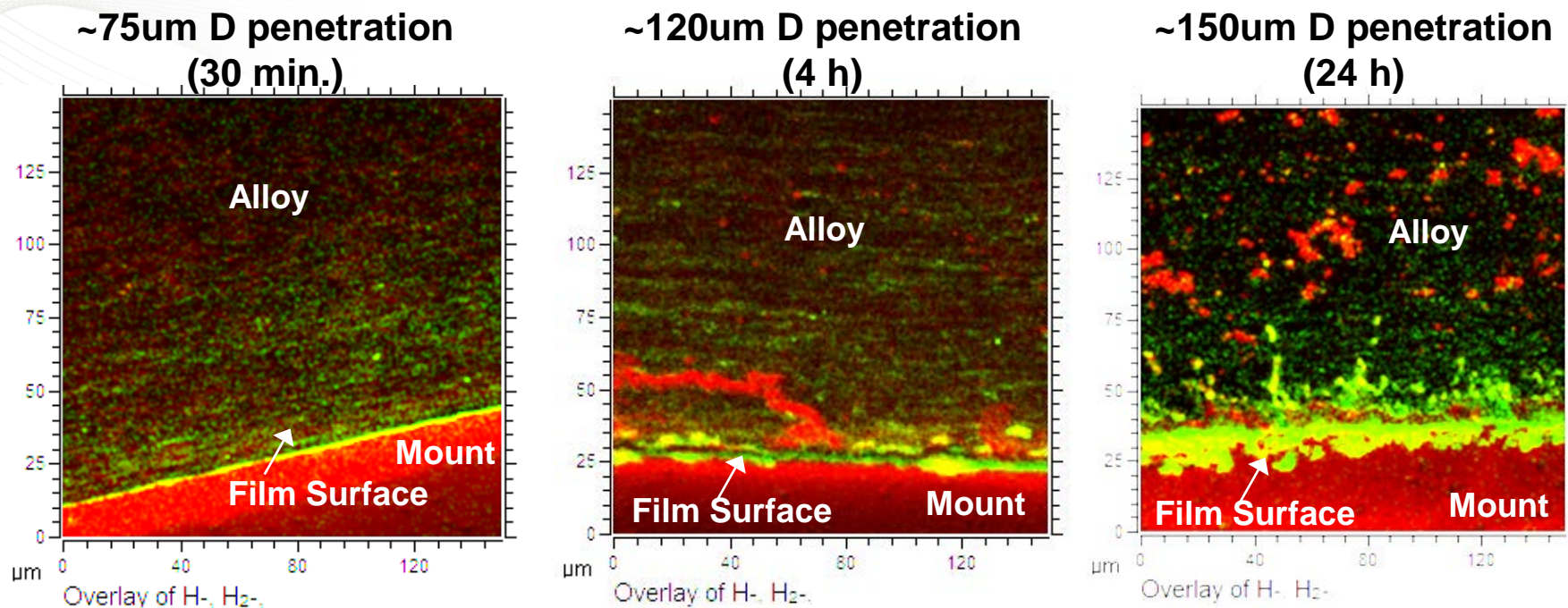
# In Progress Analysis of In-Situ SANS Data Obtained in FY2017

Reduced *in situ* small angle neutron scattering data for ZE10A and AZ31B collected at 5 min resolution for 24 h in D<sub>2</sub>O + 5 wt.% NaCl



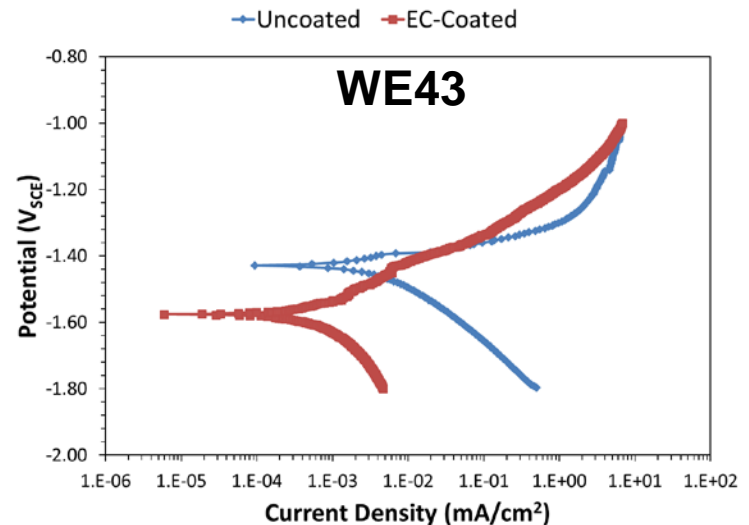
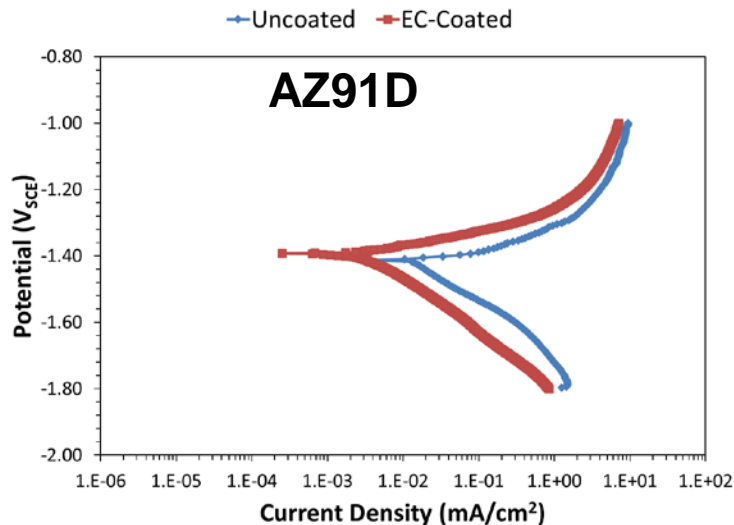
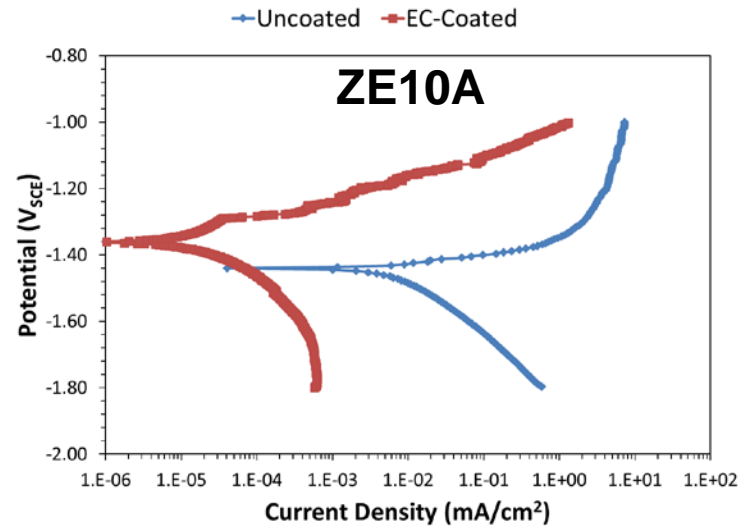
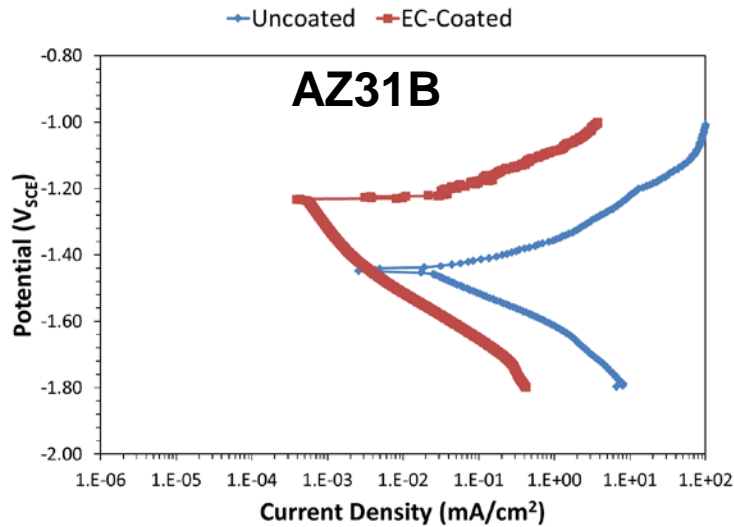
- SANS provides information on corrosion film nanoporosity (project team 2015 paper)
- Comparative ex-situ SANS data at 30 mins, 1 h, 4 h, 8 h, 24 h also obtained
- Goal is to determine if further insights result from in-situ experiments

# FY17/FY18 TOF-SIMS Cross-Section Images of ZE10A in D<sub>2</sub>O + 5 wt.% NaCl: H red, D green



- These are ex-situ controls from in-situ/ex-situ SANS study
- Similar D penetration observed for ZE10A in D<sub>2</sub>O without salt
  - Zr, RE to Mg increase D penetration (FY16, 17), but may also get D/H
- Less D penetration depth in AZ31B, no enhancement in 5 wt.% NaCl

# Potentiodynamic Polarization in 0.1M NaCl Shows Moderate Benefit of Electro-ceramic (EC) Coating



(triplicates run for all)



# Technical Progress FY18: Alloy/Electro-ceramic Interface Maintained

**STEM Bright Field Cross-Section + Elemental Maps of Exalta ES27 E-coat on Electro-ceramic coated AZ91**

